METHOD 6800

ELEMENTAL AND SPECIATED ISOTOPE DILUTION MASS SPECTROMETRY

1.0 SCOPE AND APPLICATION

1.1 This method consists of two approaches: isotope dilution mass spectrometry (IDMS) for the determination of total metals and speciated isotope dilution mass spectrometry (SIDMS) for the determination of elemental species. This method is applicable to the determination of total metals and metal species at sub µg/L levels in water samples or in waste extracts or digests. In general, elements that have more than one available stable isotope can be analyzed by IDMS. SIDMS may require more isotopes of an element, depending on the number of interconvertable species. The current method is applicable to the following elements.

Element		CASRN[a]
Antimony	(Sb)	7440-36-0
Boron	(B)	7440-42-8
Barium	(Ba)	7440-39-3
Cadmium	(Cd)	7440-43-9
Calcium	(Ca)	7440-70-2
Chromium	(Cr)	7440-47-3
Copper	(Cu)	7440-50-8
Iron	(Fe)	7439-89-6
Lead	(Pb)	7439-92-1
Magnesium	(Mg)	7439-95-4
Mercury	(Hg)	7439-97-6
Molybdenum	(Mo)	7439-98-7
Nickel	(Ni)	7440-02-0
Potassium	(K)	7440-09-7
Selenium	(Se)	7782-49-2
Silver	(Ag)	7440-22-4
Strontium	(Sr)	7440-24-6
Thallium	(TI)	7440-28-0
Vanadium	(V)	7440-62-2
Zinc	(Zn)	7440-66-6

[a] Chemical Abstracts Service Registry Number

Other elements and species may be analyzed by this method if appropriate performance is demonstrated for the analyte of interest, in the matrices of interest, at the concentration levels of interest (see Section 9.0).

1.2 Isotope dilution is based on the addition of a known amount of enriched isotope to a sample. Equilibration of the spike isotope with the natural element/species in the sample alters the isotope ratio that is measured. With the known isotopic abundance of both spike and sample, the amount of the spike added to the sample, and the altered isotope ratio, the concentration of the element/species in the sample can be calculated.

1.3 IDMS has proven to be a technique of high accuracy for the determination of total metals in various matrices (Reference 1). IDMS has several advantages over conventional calibration methodologies. Partial loss of the analyte after equilibration of the spike and the sample will not influence the accuracy of the determination. Fewer physical and chemical interferences influence the determination as they have similar effects on each isotope of the same element. The isotope ratio to be measured for quantification in IDMS can be measured with very high precision, typically RSD$\leq$0.25%.

1.4 SIDMS takes a unique approach to speciated analysis that differs from traditional methods. Traditional speciation methods attempt to hold each species static while making the measurement. Unfortunately, speciation extraction and analysis methods inherently measure the species after species conversions have occurred. SIDMS has been developed to address the correction for the species conversions. In SIDMS, each species is "labeled" with a different isotope-enriched spike in the corresponding species form. Thus, the interconversions that occur after spiking are traceable and can be corrected. While SIDMS maintains the advantages of IDMS, it is capable of correcting the degradation of the species or the interconversion between the species (Reference 2). SIDMS is also a diagnostic tool that permits the evaluation of species-altering procedures and permits evaluation and validation of other more traditional speciation analysis methods.

1.5 Both IDMS and SIDMS require the equilibration of the spike isotope(s) and the natural isotopes. For IDMS, the spike and sample can be in different chemical forms; only total elemental concentrations will result. In general, equilibration of the spike and sample isotopes occurs as a result of decomposition, which also destroys all species-specific information when the isotopes of an element are all oxidized or reduced to the same oxidation state. For SIDMS, spikes and samples must be in the same speciated form. This requires the chemical conversion of the elements in spikes. For solution samples, spiking and equilibration procedures can be as simple as mixing the known amount of the sample and the spikes. Efforts are taken to keep the species in their original species forms after spiking. While drinking water, ground water, and other aqueous samples may be directly spiked, soils, sludges, sediments, and other solid wastes require extraction or digestion prior to analysis to solubilize the elemental species.

1.6 Detection limits, sensitivity, and optimum ranges of the elements will vary with the matrix, separation method, and isotope ratio measurement methods. With the popularity of chromatography and ICP-MS, it is convenient to separate elemental species and to measure the isotope ratios. Although this method is not restricted to chromatography as the separation method of the species and the ICP-MS as the isotope ratio measurement method, this method will use these two techniques as examples in describing the procedures. Other species separation methods, such as extraction, precipitation, and solid phase chelation, and other isotope ratio measurement techniques, such as thermal ionization mass spectrometry (TIMS), can also be used.

2.0 SUMMARY OF METHOD

2.1 IDMS method:

2.1.1 Samples may require a variety of sample preparation procedures, depending on sample matrices and the isotope ratio measurement methods. One primary purpose of sample preparation is to solubilize the analyte of interest and equilibrate the spike isotopes with sample isotopes. Solids, slurries, and suspended material must be subjected to digestion after spiking using appropriate sample preparation methods (such as Method 3052). Water samples may not require digestion when ICP-MS is used as a detection method because ICP can destroy elemental species and thus many species are indistinguishable for ICP-MS.

2.1.2 A representative measured sample is thoroughly mixed with a measured amount of the isotopic spike. If a digestion procedure is required, the spiked sample is then digested to equilibrate the spikes and samples. The sample solutions are then measured with mass spectrometry such as ICP-MS to obtain the altered isotope ratios. Method 6020 can be used as a reference method for ICP-MS detection. In addition to Method 6020, dead time correction and mass bias correction must be included in the measurement protocol. The equations described in Section 12.1 are used to calculate the concentrations. Figure 2 shows an example of an IDMS determination of vanadium in crude oil (Reference 1).

2.2 SIDMS method:

2.2.1 Speciated samples generally require sample preparation specific to the sample matrices, species, and the isotope ratio measurement method. The purpose of sample preparation is to solubilize the species of interest and to equilibrate the natural and spiked species, creating a homogeneous solution. Solids, slurries, and suspended material must be subjected to extraction before spiking, using appropriate sample preparation methods (such as Method 3060 for the determination of Cr(VI) in soils). Water samples may not need extraction. In contrast to total element analysis, efforts must be taken to avoid the destruction of the species in SIDMS.

2.2.2 Although SIDMS is a general method applicable to many elements in various species forms, environmental samples, such as water samples or soil extracts, containing chromium species Cr(III) and Cr(VI) will be used for demonstration purposes. Two isotopic spikes are prepared and characterized: ^{50}Cr(III) spike enriched in ^{50}Cr and ^{53}Cr(VI) enriched in ^{53}Cr. The dominant natural isotope for Cr is ^{52}Cr, at 83.79% (^{50}Cr, 4.35%; ^{53}Cr, 9.50%; ^{54}Cr, 2.36%). A measured amount of a representative aqueous sample is mixed well with an appropriate amount of ^{50}Cr(III) and ^{53}Cr(VI) spike solutions. The spiked sample is then separated into Cr(III) and Cr(VI) using chromatography or other separation method. Four isotope ratios are measured: ^{50}Cr(III)/^{52}Cr(III), ^{53}Cr(III)/^{52}Cr(III), ^{50}Cr(VI)/^{52}Cr(VI), and ^{53}Cr(VI)/^{52}Cr(VI). The concentrations of the species are determined from speciated isotope dilution calculations. Figure 4 and Figure 5 show an example of the SIDMS for the determination of chromium species in an aqueous sample. Any transformation from Cr(VI) to Cr(III) or from Cr(III) to Cr(VI) are mathematically corrected, as described in Section 12.2.

3.0 Definitions

3.1 Isotope dilution mass spectrometry (IDMS): A quantitative method for total concentration of an analyte based on the measurement of the isotope ratio of a nuclide using mass spectrometry after isotope dilution.

3.2 Isotope dilution: Mixing of a given nuclide with one or more of its isotopes. The isotope usually has an enriched isotopic abundance different from that occurring naturally.

3.3 Speciated isotope dilution mass spectrometry (SIDMS). A quantitative method for determining elemental species based on the measurement of isotope ratio(s) in each species of a nuclide using mass spectrometry after speciated isotope dilution. Samples are mixed with one or more isotopic spikes which have different isotopic abundance and are artificially converted to chemical forms corresponding to the species to be analyzed. The spiked samples are then subjected to the separation of the species and the measurement of the altered isotope ratios in each species. Both species concentrations and species conversions can be mathematically deconvoluted.

3.4 Isotopic abundance: The relative number of atoms of a particular isotope in a mixture of the isotopes of an element, expressed as a fraction of all the atoms of the element.

3.5 Isotopes: Nuclides having the same atomic number but different mass numbers.

3.6 Species: Chemical forms in which an element exists.

3.7 Natural isotopic abundance: Isotopic abundance of elements from natural sources. Most elements (except lithium, lead and uranium) found in nature have a constant isotope abundance.

3.8 Isotope ratio: Ratio of the isotopic abundances of two isotopes.

3.9 Speciation (or speciated) analysis: Quantification of elements in specific chemical forms.

3.10 Isotope-enriched material: Material containing elements artificially enriched in minor isotopes.

3.11 Isotopic spike (Isotope-enriched spike): Standards prepared from isotope-enriched materials.

3.12 Dead time: The interval during which the detector and its associated counting electronics are unable to resolve successive pulses. The measured counts are lower than the true counts if no correction is performed.

3.13 Gain loss: The loss of gain in detector caused by the inability of the multiplier's dynode string to supply enough current to maintain constant dynode voltage drops. The measured counts are lower than the true counts, and cannot be mathematically corrected if gain loss occurs.

3.14 Mass Bias: The deviation of the measured isotope ratio from the true value caused by the differential sensitivity of the instrument to mass. This effect may occur in the ionization process or from differential transmission/detection by the mass spectrometer.

3.15 Mass bias factor: A number used to correct the mass bias of the measured isotope ratios. Mass bias factor is measured by employing an isotopically certified standard.

3.16 Isotopic-abundance-certified standard (Isotopically certified standard): Standard material with certified isotopic abundance.

3.17 Inverse isotope dilution: Analysis method to determine the concentrations of isotopic spikes. A known quantity and isotopic abundance of an isotopic spike is mixed with a known amount and isotopic abundance (usually tabulated natural isotopic abundance or certified isotopic abundance) of standard(s), and the altered isotope ratio(s) is(are) measured and used in the calculation to find the concentration of the isotopic spike. Usually, a natural material is used to calibrate and determine the concentration of the separated isotopic spike solution using this method. Only in the case of such elements as uranium, lead, and lithium are the natural isotopic abundances not constant in terrestrial materials.

3.18 Single spiking: Addition of one isotopic spike to the sample.

3.19 Double spiking: Addition of two isotopic spikes to the sample. The two isotopic spikes are enriched in different isotopes, and are prepared in different chemical forms, each of which corresponds to a species form.

3.20 Unidirectional conversion: One directional transformation occurring between two species. One species can convert to the other; the reverse transformation does not occur.

3.21 Interconversion: Bi-directional transformation occurring between two species. Species convert back and forth between the two chemical forms.

3.22 Time resolved analysis (TRA): A data collection mode in which the data can be acquired at specified intervals for a continuously aspirated sample, over a user-defined period of time.

4.0 INTERFERENCES

4.1 Sample preparation

4.1.1 Because this method requires the equilibration of the spike isotope(s) and the natural isotopes, the sample must be digested, dissolved or extracted into a solution. If the analyte of interest does not completely dissolve, if the spike or sample isotopes are selectively lost before equilibration, or if contamination occurs in the sample preparation process, the measured isotope ratio will not reflect the accurate ratio of added spike atoms to sample atoms for that element or species (Reference 1).

4.1.2 In general, SIDMS incorporates the assumption that all the converted species can be found in other species that are monitored. As an example, in the interconversion between Cr(III) and Cr(VI), the lost Cr in one species must be found in the other species. Thus, efforts should be made to keep all species in solution.

4.1.3 Preservation of the species is required in SIDMS since the interconversion degrades the precision of the determination. The complete conversion of the species will disable the deconvolution of the species concentration. Thus, digestion methods used for total metals are inappropriate for SIDMS. However, the altered isotope ratios will indicate the conversion that has occurred and will not lead to an incorrect answer, but to a situation where the concentration cannot be determined. Approaches that have been developed to maintain the species are applicable to SIDMS.

4.2 Isotope ratio measurement

4.2.1 Discussions about isobaric interference, doubly-charged ion interference, and memory interference in Method 6020 are applicable to this method. The discussion about the physical interference, suggesting the addition of an internal standard, does not apply. The internal standard is unnecessary because the isotope ratio measurement is free from physical interferences. (General considerations for isotope ratio measurement can be found in the document of Section 13.3.1).

4.2.2 Dead time measurement must be performed daily. At high count rates, two effects cause pulse counting systems to count less events than actually occur (Section 13.3.2). The first is dead time (t), the interval during which the detector and its associated counting electronics are unable to resolve successive pulses. If the true rate, n, is much less than $1/t$, then:

$$m \approx n(1-n\tau)$$

where *m* is the observed rate. The second effect is the loss of gain at high rates caused by the inability of the multiplier's dynode string to supply enough current to maintain constant dynode voltage drops. This effect is indicated by a sharp increase in apparent dead time at high count rates. Both effects cause the measured isotope ratios to diverge from the true isotope ratios with increasing count rate. While the dead time can be mathematically corrected, the gain loss cannot.

A series of solutions with different concentrations can be prepared from isotopically certified standards for the determination of dead time. The concentrations may not be accurate, but the concentrations should spread out evenly, covering the blank to the highest count rate that may be used in measurements. The isotope pairs that are monitored should have large differences between their isotopic abundances, since the major isotopes suffer dead time effects much more seriously than minor isotopes; this makes the dead time correction significant. The sum of the dead-time-corrected counts is used for calculating the isotope ratios after background subtraction.

$$R_m = \frac{{}^{\text{Isotope1}}S_{\text{sample/standard}} - {}^{\text{Isotope1}}S_{\text{background}}}{{}^{\text{Isotope2}}S_{\text{sample/standard}} - {}^{\text{Isotope2}}S_{\text{background}}}$$

- R_m is the dead-time-corrected isotope ratio;
- ${}^{\text{Isotope1}}S_{\text{sample/standard}}$ and ${}^{\text{Isotope2}}S_{\text{sample/standard}}$ and are the integrated dead-time-corrected-counts for the sample or standard of Isotope1 and Isotope2, respectively;
- ${}^{\text{Isotope1}}S_{\text{background}}$ and ${}^{\text{Isotope2}}S_{\text{background}}$ are the integrated dead-time-corrected-counts for the background of Isotope1 and Isotope2, respectively.

As shown in Figure 1, which displays the $^{50}Cr/^{52}Cr$ ratios for SRM 979 ($Cr(NO_3)_3 \bullet 9H_2O$) as a function of the count rate, the isotope ratios are highly dependent on the number used for dead time correction. When the dead time is set to 43.5 ns, the isotope ratios are approximately constant up to the count rate of 5.8×10^5. At higher count rates, gain loss will occur and cannot be mathematically corrected. Therefore, the solutions must be diluted in the case where the count rate is higher than this value.

NOTE: Dead time correction is performed before mass bias correction, so the dead-time-corrected isotope ratios may be different from the certified isotope ratios. Although it is unnecessary to use isotopically certified material for the determination of dead time, the certified material is still required for the measurement of mass bias factors. Thus, it is convenient to use the same certified material for both dead time and mass bias factor measurement.

NOTE: It has been observed that using different isotope pairs for dead time measurement may obtain different dead times. Thus, it is required to do the dead time measurement for each isotope pair that will be used. The dead time must be determined daily.

4.2.3 Instrumental discrimination/fraction effects are changes induced in the "true" isotope ratios from the ionization process or from differential transmission/detection by the mass spectrometer. This effect can bias the ratios either positively or negatively. To correct the mass bias, mass bias factors should be determined with isotopically certified materials.

$$\text{mass bias factor} = R_t / R_m$$

where:

- R_t and R_m are the certified isotope ratio and the measured dead-time-corrected-isotope-ratios of the standard material.

The dead-time-corrected isotope ratios of the samples can be corrected using:

$$R_c = \text{mass bias factor} \times R_m$$

where:

- R_c and R_m are the corrected isotope ratio and the measured dead-time-corrected-isotope-ratios of the sample, respectively.

Mass discrimination is a time-dependent instrumental effect, so the mass bias factors must be determined periodically during the measurement of the samples. Samples are run with the assumption that mass bias factors remain constant. In general, the mass bias factors are stable over several hours for ICP-MS measurements.

NOTE: Some previous work observed the following relationship between the measured and the true isotope ratios for ICP-MS: $R_m=R_t(1+an)$, where a is the bias per mass unit, n is the mass difference between isotopes. This enables the calculation of the mass bias factors of other isotope pairs based on the measurement of one pair of isotopes. However, this must be verified experimentally. Otherwise, the mass bias factor for each isotope pair must be determined.

5.0 SAFETY

5.1 Refer to Chapter Three for a discussion on safety related references and issues.

5.2 Many chromium compounds are highly toxic if swallowed, inhaled, or absorbed through the skin. Extreme care must be exercised in the handling of hexavalent chromium reagents. Hexavalent chromium reagents should only be handled by analysts who are knowledgeable of their risks and of safe handling procedures.

6.0 EQUIPMENT AND SUPPLIES

6.1 Inductively coupled plasma-mass spectrometer (ICP-MS) or other mass spectrometer systems capable of base line (at least 1 amu) resolution are required. The data system should allow for corrections of isobaric interferences, dead time and mass bias, or the raw data may be exported to a computer for further processing. For quadrupole mass spectrometers, the dwell time should be adjustable since proper settings of dwell time can significantly improve the precision of the isotope ratio measurement. Both scan mode and peak jump mode can be used, depending on the instrumentation. The use of a mass-flow controller for the nebulizer argon and a peristaltic pump for the sample solution are recommended. When chromatography is coupled to ICP-MS for on-line

detection, the ICP-MS data system must be capable of correcting interferences, dead time and mass bias, and calculating the isotope ratios in time resolved analysis mode (TRA), or the raw data can be exported for off-line processing. Other mass spectrometers may also be used, providing a precision of 0.5% or better can be obtained for the isotope ratio measurement.

6.2 Chromatography or other separation methods are used to isolate species prior to isotope ratio measurement. Chromatography, such as ion exchange chromatography, may be used to separate the species on-line in SIDMS (Figure 3). Chromatography components should be chemically inert based on the specific reagents and analytes. The eluent components and the flow rate of the chromatography system must be compatible with ICP-MS. An interface between the chromatography and ICP-MS may be required for compatibility reasons. Alternatively, any appropriate separation methods, including extraction, chelation, and precipitation, can be used after validation.

7.0 REAGENTS AND STANDARDS

7.1 All reagents should be of appropriate purity to minimize the blank levels due to contamination. Whenever possible, acids should be sub-boiling distilled. All references to water in the method refer to high purity reagent water. Other reagent grades may be used if it is first ascertained that the reagent is of sufficient purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is questionable, analyze the reagent to determine the level of impurity.

7.2 For higher precision, solutions may be prepared by weight. For IDMS, standard stock solutions with natural isotopic abundance may be purchased or prepared from ultra-high purity grade chemicals or metals. See Method 6010 for instruction on preparing standard solutions from solids. Generally, the same procedures are applicable to isotope-enriched materials. However, when a limited amount of the isotope-enriched material is used (usually due to cost considerations) to prepare the stock solutions, the solutions require calibration with inverse isotope dilution (Section 7.4.1). Isotope-enriched materials with known enrichment can be purchased from several suppliers, such as the Oak Ridge National Laboratory Electromagnetic Isotope Enrichment Facility (ORNL-EMIEF).

7.3 Currently, few standard stock solutions made for speciation analysis are commercially available. Thus, in addition to the dissolution of the standard solid, the chemical conversion of the element into the desired species is usually required for SIDMS. The preparation of Cr(VI) and Cr(III) stock standards for SIDMS will be illustrated as an example. For other elements and species, procedures must be specifically developed.

7.3.1 There are five standards to be prepared for the simultaneous analysis of Cr(VI) and Cr(III), including ^{nat}Cr(VI) and ^{nat}Cr(III) with natural abundance, ^{53}Cr(VI) enriched in ^{53}Cr, ^{50}Cr(III) enriched in ^{50}Cr, and isotopic-abundance-certified Cr standard solution.

7.3.2 1 mg/mL Cr(VI) and Cr(III) standards are commercially available. ^{nat}Cr(VI) and ^{nat}Cr(III) can also be prepared from $K_2Cr_2O_7$ and Cr metal, respectively.

7.3.2.1 ^{nat}Cr(VI) standard solution, stock, 1 g = 1 mg Cr: Dissolve 0.2829 grams of $K_2Cr_2O_7$ in about 80 mL of reagent water and dilute to 100 g with reagent water.

7.3.2.2 $^{nat}Cr(III)$ standard solution, stock, 1 g = 1 mg Cr: Dissolve 0.1 g Cr metal in a minimum amount of 6M HCl and dilute the solution with 1% HNO_3 to 100 grams.

7.3.3 $^{53}Cr(VI)$ standard solution, 1 g ≈ 10 µg Cr: The following procedure describes chromium oxide as the source material. A 150 mL glass or quartz beaker is used for the dissolution. Weigh 5.8 mg (the exact amount should be calculated based on the content of Cr in the material) ^{53}Cr-enriched oxide into the beaker and add 8 mL concentrated $HClO_4$. Slowly heat the beaker on a hot plate until bubbles form on the bottom; the solution should not boil. Keep heating the solution for up to 6 hours until all solids are dissolved and only 1 to 2 mL of the solution remains. Turn off the hot plate and wait until the beaker cools down. Rinse the beaker and watch glass with 10 mL reagent water; the solution should turn intense yellow. Add 50 µL of 30% H_2O_2 and 4.5 mL of concentrated NH_4OH. Slowly heat the vessel until the solution gently boils to oxidize all Cr to Cr(VI). Allow the solution to boil for at least 15 minutes to remove the excessive H_2O_2. Transfer the solution to a 500 mL polymeric (Teflon, polyethylene, polypropylene, etc.) bottle and dilute the solution to 400 g. The exact concentration of the $^{53}Cr(VI)$ spike must be calibrated with $^{nat}Cr(VI)$ standard as described in Section 7.4.

NOTE: The procedure may be simpler when the isotope-enriched materials are available in other forms. For example, when $K_2Cr_2O_7$ enriched in ^{53}Cr is available, the solid can be dissolved in reagent water without further conversion; when Cr metal is available, the metal can be dissolved in 6M HCl as described in Section 7.3.2.2, followed by the addition of H_2O_2 and NH_4OH to oxidize Cr(III) to Cr(VI) as described above.

CAUTION: Concentrated $HClO_4$ is a very strong oxidizer. Safety protocols require this reagent only be used in a perchloric acid hood or equivalent solution and vapor handling system.

7.3.4 $^{50}Cr(III)$ standard solution, 1 g ≈ 10 µg Cr: The following procedure describes chromium metal as the source material. Weigh 4 mg of the metal into a 30 mL Teflon vessel. Add 4 mL of 6M HCl and gently heat the solution but do not boil it until the solid is dissolved. Continue to heat the solution until only 1 to 2 mL of the solution remains. The solution is then cooled and transferred to a 500 mL polymeric bottle. Dilute the solution with 1% HNO_3 to 400 grams. The exact concentration of the $^{50}Cr(III)$ spike must be calibrated with ^{nat}Cr standard as described in Section 7.4.

NOTE: The procedure depends on the form of the material. For example, when $K_2Cr_2O_7$ enriched in ^{50}Cr is available, the solid can be dissolved in 1% HNO_3, followed by the addition of H_2O_2 to reduce Cr(VI) to Cr(III). The excessive H_2O_2 can be removed by boiling the solution.

7.3.5 Isotopic-abundance-certified standard solution, stock, 1 g ≈ 10 µg Cr: Weigh 31 mg $Cr(NO_3)_3 \bullet 9H_2O$ (SRM 979) into a 500 mL polymeric container. Dissolve the solid and dilute it with 1% HNO_3 to 400 g.

7.4 The isotope-enriched spikes require characterization since a limited amount of material is usually weighed, complex treatment is involved, or the purity of the source material is limited (frequently <99%). For the SIDMS method, in addition to the total concentration of the standard, the distribution of the species must be determined before it can be used. Inverse IDMS and inverse

SIDMS measurement is used to calibrate the isotope-enriched spike and to determine the species distribution. The characterization of $^{53}Cr(VI)$ spike solution will be illustrated as an example.

7.4.1 Calibration of total concentration of spike solution with natural material: Weigh the proper amount (W_X) of 10 µg/g ($C_{Standard}$) ^{nat}Cr standard and the proper amount (W_S) of the $^{53}Cr(VI)$ spike (nominal concentration is 10 µg/g) into a polymeric container, and dilute the mixture with 1% HNO_3 to a concentration suitable for isotope ratio measurement. Use direct aspiration mode to determine the isotope ratio of $^{53}Cr/^{52}Cr$ ($R_{53/52}$). The concentration of the spike, C_{Spike} , can be calculated using the following equations.

$$C_{Spike} = C_S M_S$$

$$C_S = \frac{C_X W_x}{W_S} \left(\frac{{}^{53}A_X - R_{53/52}\,{}^{52}A_X}{R_{53/52}\,{}^{52}A_S - {}^{53}A_S} \right)$$

$$C_X = C_{standard} / M_X$$

where, C_S and C_X are the concentrations of the isotope-enriched spike and the standard with natural isotopic abundance in mmole/g, respectively. M_S and M_X are the average atomic weights of the spike and the standard in g/mol, respectively. $^{53}A_S$ and $^{53}A_X$ are the atomic fractions of ^{53}Cr for the spike and standard, respectively. $^{52}A_S$ and $^{52}A_X$ are the atomic fractions of ^{52}Cr for the spike and standard, respectively.

NOTE: The same procedure is applicable to the calibration of the isotope-enriched spike solutions in IDMS. The same procedure is also applicable to the calibration of $^{50}Cr(III)$ by changing isotope ^{53}Cr to ^{50}Cr.

NOTE: Average atomic weight = Σ(atomic weight of the isotope x atomic fraction)

7.4.2 Calibration of the concentration of the Cr(VI) in the $^{53}Cr(VI)$ spike with $^{nat}Cr(VI)$: Weigh the proper amount (W_X) of 10 µg/g ($C^{VI}_{standard}$) $^{nat}Cr(VI)$ standard and the proper amount (W_S) of the $^{53}Cr(VI)$ spike (nominal concentration is 10 µg/g) into a polymeric container, and dilute the mixture with reagent water to a concentration suitable for measurement. Acidify the solution to pH 1.7-2.0 with concentrated HNO_3. Separate the Cr(VI) with chromatography or other separation methods and measure the isotope ratio of $^{53}Cr/^{52}Cr$ in Cr(VI) species ($R^{VI}_{53/52}$). The concentration of Cr(VI) in the spike, C^{VI}_{Spike}, can be calculated using the following equations.

$$C_{Spike}^{VI} = C_S^{VI}\ M_S$$

$$C_S^{VI} = \frac{C_X^{VI}\ W_x}{W_S}\left(\frac{{}^{53}A_X - R_{53/52}^{VI}\ {}^{52}A_X}{R_{53/52}^{VI}\ {}^{52}A_S - {}^{53}A_S}\right)$$

$$C_X^{VI} = C_{Standard}^{VI}\ /M_X$$

where, C_S^{VI} and C_X^{VI} are the concentrations of Cr(VI) in the isotope-enriched spike and standard with natural isotopic abundance in µmole/g, respectively. M_S and M_X are the average atomic weights of the spike and the standard in g/mol, respectively. ${}^{53}A_S$ and ${}^{53}A_X$ are the atomic fractions of ^{53}Cr for the spike and standard, respectively. ${}^{52}A_S$ and ${}^{52}A_X$ are the atomic fractions of ^{52}Cr for the spike and standard, respectively.

NOTE: This set of equations is similar to those used in the determination of total Cr in ^{53}Cr(VI) standard (Section 7.4.1). The general equations for inverse SIDMS are not so simple. However, for speciation of Cr(VI) and Cr(III) in standard solutions, because the matrix is so simplified, only the reduction of Cr(VI) to Cr(III) is observed at low pH. Thus, the existence of Cr(III) species will not influence the isotope ratio of Cr(VI), and the complex equations can be simplified to the equations shown above (Reference 3).

7.4.3 The distribution of Cr(III) and Cr(VI) in ^{53}Cr(VI) spike can be calculated as:

$$\text{percentage of Cr(VI)} = \frac{C_{Spike}^{VI}}{C_{Spike}} \times 100\%$$

$$\text{percentage of Cr(III)} = \left(1 - \frac{C_{Spike}^{VI}}{C_{Spike}}\right) \times 100\%$$

NOTE: No determination of the species distribution in ^{50}Cr(III) spike is required because only Cr(III) is present in this solution.

7.5 Blanks: Three types of blanks are required for the analysis: background blank for subtracting background in isotope ratio measurement, preparation blank for monitoring possible contamination resulting from the sample preparation procedures, and rinse blank for flushing the system between all samples and standards.

7.5.1 The background blank consists of the same concentration(s) of the acid(s) used to prepare the final dilution of the sample solution (often 1% HNO_3 (v/v) in reagent water).

7.5.2 The preparation (or reagent) blank must be carried through the complete preparation procedure and contain the same volumes of reagents as the sample solutions.

7.5.3 The rinse blank consists of 1 to 2 % HNO_3 (v/v) in reagent water. Prepare a sufficient quantity to flush the system between standards and samples. Refer to Method 6020 for interference check solution.

7.6 Refer to Method 6020 for preparing mass spectrometer tuning solution.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

8.2 Due to the possible degradation or interconversion of the species, samples collected for speciation analysis must be isotopically spiked as soon as possible. The measurement, however, can be carried out later provided that less than 80% degradation or interconversion occurs. The holding time prior to measurement depends on the preservation of the species.

8.3 Proper methods to retard the chemical activity of the species are applicable to SIDMS.

8.4 All sample containers must be prewashed with detergents, acids, and water. Polymeric containers should be used. See Chapter Three of this manual for further information on clean chemistry procedures to reduce blank effects in these measurements.

9.0 QUALITY CONTROL

9.1 All quality control data must be available for reference or inspection. This method is restricted to use by, or under supervision of, experienced analysts. Refer to the appropriate section of Chapter One for additional quality control guidance.

9.2 Duplicate samples should be processed on a routine basis. A duplicate sample is a sample processed through the entire sample preparation and analytical procedure. A duplicate sample should be processed with each analytical batch or every 20 samples, whichever is the greater number. A duplicate sample should be prepared for each matrix type (i.e., soil, sludge, etc.).

9.3 Spiked samples and/or standard reference materials should be included with each group of samples processed or every 20 samples, whichever is the greater number. A spiked sample should also be included whenever a new sample matrix is being analyzed. For SIDMS, because the species may degrade or convert to other species when they are spiked into samples, low recovery may be observed. Thus, the low recovery does not immediately invalidate this method. For example, if Cr(III) is spiked into a basic solution, due to the hydrolysis of Cr(III) and the limited solubility of chromium hydroxide, low recovery of Cr(III) will be obtained. Low recovery may indicate an unfavorable matrix for preserving the corresponding species (Reference 4).

9.4 Blank samples should be prepared using the same reagents and quantities used in sample preparation, placed in vessels of the same type, and processed with the samples.

10.0 CALIBRATION AND STANDARDIZATION

10.1 IDMS calibration:

10.1.1 Follow the appropriate sections in Method 6020 to set up and tune the ICP-MS. The determination is performed in direct aspiration mode. The following procedure is illustrated with the measurement of $^{50}Cr/^{52}Cr$ and $^{53}Cr/^{52}Cr$ isotope ratios.

10.1.2 Determine the dead time (Section 4.2.2). Solutions prepared from reference material SRM 979 ($Cr(NO_3)_3 \bullet 9H_2O$) are used in this determination. A range of solutions of different concentrations should be prepared, but do not need to be accurately known. Masses 50, 52 and 53, as well as masses which could affect data quality should be monitored. The raw count rates for each solution are measured and integrated. Assume a dead time and use the equation described in Section 4.2.2 to correct the integrated counts. The dead-time-corrected counts are then used for calculating the isotope ratios after background subtraction. By trial and error, the dead time is determined to bring the isotope ratios obtained from solutions of different concentrations to a constant (the relative standard deviation of the isotope ratios reach the minimum). The isotope ratios obtained from high counts may be excluded as gain loss may occur.

NOTE: The concentration range of the solutions may be adjusted depending on the sensitivity and dynamic range of the instrument.

NOTE: For direct aspiration mode, the dead time correction can be done either before or after the integration of the raw data. However, it is simpler to do the dead time correction after the integration.

10.1.3 Determine the mass bias factor (Section 4.2.3). The mean of isotope ratios obtained in Section 10.1.2 is used for calculating the mass bias factor. The equation is provided in Section 4.2.3. The measurement of the mass bias factor must be done periodically between sample measurements. The interval between these measurements depends on the mass bias stability of the instrument. The relative difference between two consecutive mass bias factors should not exceed 1%.

10.2 SIDMS calibration:

10.2.1 Follow the appropriate sections in Method 6020 to set up and tune the ICP-MS. Follow Section 10.1.2 to measure the dead time. If the calibration of the isotope-enriched spikes is required, the mass bias factors for direct aspiration mode and the altered isotope ratios for the spiked standards are measured at this step. The measured isotope ratios obtained at this step are used in the calibration of total concentrations.

10.2.2 Determine the mass bias factor (Section 4.2.3). Connect the chromatography outlet to the nebulizer of the ICP-MS. Stabilize the entire system. Background blank and an isotopic abundance certified standard are used for the measurement of the mass bias factors for TRA mode. The raw data at each point are corrected for dead time using the equation described in Section 4.2.2 and then integrated by summing the data across each peak. The intervals between two consecutive injections must be long enough for the signal to return to baseline. The integrated counts are then used to calculate the isotope ratios with the equation shown in Section 4.2.2. Apply the equation in Section 4.2.3 to the calculation of the mass bias factors for each isotope pair by comparing the measured isotope ratios to the certified isotope ratios.

NOTE: For the TRA mode, the dead time correction must be done at each data point before the data integration.

11.0 PROCEDURE

11.1 IDMS

11.1.1 Closed-vessel microwave digestion is used as an example method to decompose, solubilize and stabilize the elements of interest. The following procedure is applicable to samples specified in Method 3052. Refer to Method 3052 for specification of the microwave apparatus.

11.1.2 Prepare the isotope-enriched spike and calibrate it with the inverse isotope dilution mass spectrometry procedure described in Sections 7.2 and 7.4.1.

11.1.3 Weigh a representative sample to the nearest 0.001 g into an appropriate microwave digestion vessel equipped with a pressure relief mechanism. Spike the sample with the calibrated isotope-enriched spike. The concentration of the spike should be high enough so that only a small volume of the solution is used. At least three significant figures should be maintained for the mass of the spike.

11.1.4 Digest the sample according to the procedure described in Method 3052.

NOTE: For filtered and acidified aqueous samples, digestion may not be required. Sample solutions can be directly analyzed with ICP-MS after spiking and equilibration.

11.1.5 Measurement of the isotope ratios can be carried out using ICP-MS or other appropriate mass spectrometers.

11.1.5.1 Determine the mass bias factor periodically as described in Section 10.1.3.

11.1.5.2 Measure the isotope ratio of each sample. Flush the system with the rinse blank. The ideal isotope ratio is 1:1. Isotope ratios must be within the range from 0.1:1 to 10:1, except for blanks and samples with extremely low concentrations. Samples must be diluted if too high a count rate is observed to avoid gain loss of the detector.

NOTE: For elements such as lithium, lead, and uranium, the unspiked solution is used to measure the isotopic abundance of all the isotopes because the isotopic abundances of these elements are not invariant in nature.

11.2 SIDMS:

11.2.1 SIDMS is currently applicable to the quantification of elemental species in various aqueous solutions. Solid samples require isolation and separation to solubilize the elemental species before spiking. Procedures for such extraction of the species from different matrices must be specifically designed. The following procedure is an illustration of the simultaneous determination of Cr(III) and Cr(VI) in water samples or soil or sediment extracts. Solids are extracted for Cr(VI) using Method 3060.

11.2.2 Prepare the isotope-enriched spikes in species forms and calibrate them with inverse isotope dilution mass spectrometry described in Section 7.4.

11.2.3 Extract the species from the samples such as soils and sludges. Proposed Method 3060 can be used to extract Cr(VI) from soils.

NOTE: For aqueous samples, extraction may not be required.

11.2.4 Weigh a proper amount of water sample or extract to the nearest 0.0001 g into a polymeric container. Spike the sample with 10 µg/g ^{53}Cr(VI) spike to a concentration so that the isotope ratio of $^{53}Cr/^{52}Cr$ in Cr(VI) will be approximately 1:1. Thoroughly mix the spike and the sample. The isotope ratios $^{53}Cr/^{52}Cr$ for samples must be within the range of 0.1:1 to 10:1, except for blanks or samples with extremely low concentrations.

11.2.5 Dilute the ^{53}Cr(VI)-spiked sample with reagent water. If the solution is strongly basic, neutralize the sample with concentrated HNO_3 to avoid the hydrolysis of Cr(III). Spike the diluted sample with 10 µg/g ^{50}Cr(III) spike to a concentration so that the isotope ratios of $^{50}Cr/^{52}Cr$ in Cr(III) will also be approximately 1:1 and the species concentrations are suitable for measurement. The measured isotope ratios $^{50}Cr/^{52}Cr$ for samples must be within the range of 0.1:1 to 10:1 except for blanks and samples with extremely low concentrations, or the sample should be respiked and analyzed. (Sections 11.2.4 and 11.2.5 should be completed as quickly as possible.)

NOTE: If only the Cr(VI) is of interest, the sample can be single spiked with ^{53}Cr(VI) instead of double-spiking with both ^{50}Cr(III) and ^{53}Cr(VI). However, this is based on the assumption that only unidirectional conversion, the reduction Cr(VI) to Cr(III), can occur after spiking. This is usually true if the sample is acidified to low pH after spiking, especially for matrices containing reducing agents.

11.2.6 Acidify the spiked samples to pH 1.7 to 2.0; under these conditions Cr is usually retained in the solutions, (although there might be interconversion between Cr(III) and Cr(VI)). The spiked samples can be stored at 4°C to retard the interconversion of the species. Other methods that can retard the transformation of the species are applicable as long as no interference with the isotope ratio measurement is introduced. For example, some soil extracts contain large concentrations of reducing agents that reduce Cr(VI) rapidly after acidification. To slow down the reduction, stoichiometric amounts of $KMnO_4$ can be added to the sample to compete with Cr(VI) in the oxidation of reducing matrices.

NOTE: Studies have shown that the lower the interconversion, the more precise the determination (Reference 3). Thus, efforts should be made to prevent interconversion between the species.

11.2.7 The measurement of the isotope ratios in each species can be carried out using ICP-MS or other equivalent mass spectrometers following the separation of the species using chromatography or other separation methods. An ion-exchange chromatograph coupled with ICP-MS will be illustrated as an example in the measurement of $^{50}Cr/^{52}Cr$ and $^{53}Cr/^{52}Cr$ isotope ratios in both Cr(III) and Cr(VI) species in samples.

11.2.7.1 Determine the mass bias factors periodically as described in Section 10.2.2.

11.2.7.2 Measure the isotope ratios of each sample. Flush the system with the eluent until the signal returns to the baseline. The ideal isotope ratios for $^{50}Cr/^{52}Cr$ in Cr(III) and $^{53}Cr/^{52}Cr$ in Cr(VI) are 1:1. Ratios between 0.1:1 to 10:1 are also acceptable. Samples may be respiked to achieve an isotope ratio close to 1:1. Samples must be diluted if excessively high count rates are observed to avoid gain loss of the detector.

NOTE: For elements such as lithium, lead, and uranium, the unspiked solution is used to measure the isotopic abundance of all the isotopes because the isotopic abundances are not invariant in nature.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 IDMS-Calculations: The quantitative values shall be reported in appropriate units, such as micrograms per liter (µg/L) for aqueous samples and milligrams per kilogram (mg/kg) for solid samples. If dilutions are performed, the appropriate corrections must be applied to the sample values.

12.1.1 Calculate the isotope ratios. Calculations should include appropriate interference corrections (see Section 4.2 for data integration, dead time correction, and mass bias correction).

12.1.2 The following equations are applied to the calculation of the concentration of the element, C_{Sample}(µg/g), in the final sample solutions.

$$C_{Sample} = C_X M_X$$

$$C_S = C_{Spike} / M_S$$

$$C_X = \frac{C_S W_S}{W_X} \left(\frac{{}^{53}A_S - R_{53/52}\,{}^{52}A_S}{R_{53/52}\,{}^{52}A_X - {}^{53}A_X} \right)$$

where, C_S and C_X are the concentrations of the isotope-enriched spike and the sample in mmole/g, respectively. M_S and M_X are the average atomic weights of the isotope-enriched spike and the sample in g/mole, respectively. $^{53}A_S$ and $^{53}A_X$ are the atomic fractions of ^{53}Cr for the isotope-enriched spike and sample, respectively. $^{52}A_S$ and $^{52}A_X$ are the atomic fractions of ^{52}Cr for the isotope-enriched spike and sample, respectively. C_{spike} is the concentration of the isotope-enriched spike in µg/g.

NOTE: When isotope ^{50}Cr is used, substitute 53 with 50 in the above equations.

12.1.3 If appropriate or required, calculate results for solids on a dry-weight basis as follows:

(1) A separate determination of percent solids must be performed.
(2) The concentrations determined in the digest are to be reported on the basis of the dry weight of the sample.

$$\text{Concentration (dry weight)(mg/kg)} = \frac{C_{Sample}}{S}$$

where, C_{Sample} = Concentration based on the wet sample (µg/g)

$$S = \frac{\%\ \text{Solids}}{100}$$

12.2 SIDMS-Calculations: The quantitative values shall be reported in appropriate units, such as micrograms per liter (µg/L) for aqueous samples and milligrams per kilogram (mg/kg) for solid samples. If dilutions are performed, the appropriate corrections must be applied to the sample values.

12.2.1 Calculate the isotope ratios. Calculations should include appropriate interference corrections, dead time correction, and mass bias correction (Section 4.2).

12.2.2 The following equations are used to deconvolute the concentrations of the species at the time of spiking, as well as the conversion of the species after spiking.

$$R^{III}_{50/52} = \frac{\left({}^{50}A_x C_x^{III} W_x + {}^{50}A_s^{III} C_s^{III} W_s^{III}\right)(1-\alpha) + \left({}^{50}A_x C_x^{VI} W_x + {}^{50}A_s^{VI} C_s^{VI} W_s^{VI}\right)\beta}{\left({}^{52}A_x C_x^{III} W_x + {}^{52}A_s^{III} C_s^{III} W_s^{III}\right)(1-\alpha) + \left({}^{52}A_x C_x^{VI} W_x + {}^{52}A_s^{VI} C_s^{VI} W_s^{VI}\right)\beta}$$

$$R^{III}_{53/52} = \frac{\left({}^{53}A_x C_x^{III} W_x + {}^{53}A_s^{III} C_s^{III} W_s^{III}\right)(1-\alpha) + \left({}^{53}A_x C_x^{VI} W_x + {}^{53}A_s^{VI} C_s^{VI} W_s^{VI}\right)\beta}{\left({}^{52}A_x C_x^{III} W_x + {}^{52}A_s^{III} C_s^{III} W_s^{III}\right)(1-\alpha) + \left({}^{52}A_x C_x^{VI} W_x + {}^{52}A_s^{VI} C_s^{VI} W_s^{VI}\right)\beta}$$

$$R^{VI}_{50/52} = \frac{\left({}^{50}A_x C_x^{III} W_x + {}^{50}A_s^{III} C_s^{III} W_s^{III}\right)\alpha + \left({}^{50}A_x C_x^{VI} W_x + {}^{50}A_s^{VI} C_s^{VI} W_s^{III}\right)(1-\beta)}{\left({}^{52}A_x C_x^{III} W_x + {}^{52}A_s^{III} C_s^{III} W_s^{III}\right)\alpha + \left({}^{52}A_x C_x^{VI} W_x + {}^{52}A_s^{VI} C_s^{VI} W_s^{VI}\right)(1-\beta)}$$

$$R^{VI}_{53/52} = \frac{\left({}^{53}A_x C_x^{III} W_x + {}^{53}A_s^{III} C_s^{III} W_s^{III}\right)\alpha + \left({}^{53}A_x C_x^{VI} W_x + {}^{53}A_s^{VI} C_s^{VI} W_s^{III}\right)(1-\beta)}{\left({}^{52}A_x C_x^{III} W_x + {}^{52}A_s^{III} C_s^{III} W_s^{III}\right)\alpha + \left({}^{52}A_x C_x^{VI} W_x + {}^{52}A_s^{VI} C_s^{VI} W_s^{VI}\right)(1-\beta)}$$

where,

$R^{III}_{50/52}$ is the measured isotope ratio of ^{50}Cr to ^{52}Cr of Cr(III) in the spiked sample

$^{50}A_X$ is the atomic fraction of ^{50}Cr in the sample (usually a constant in nature)

C^{III}_X is the concentration of Cr(III) in the sample (µmole/g, unknown)

W_X is the weight of the sample (g)

$^{50}A^{III}_S$ is the atomic fraction of ^{50}Cr in the ^{50}Cr(III) spike

C^{III}_S is the concentration of Cr(III) in the ^{50}Cr(III) spike (µmole/g)

W^{III}_S is the weight of the ^{50}Cr(III) spike (g)

C^{VI}_X is the concentration of Cr(VI) in the sample (µmole/g, unknown)

α is the percentage of Cr(III) oxidized to Cr(VI) after spiking (unknown)

β is the percentage of Cr(VI) reduced to Cr(III) after spiking (unknown)

NOTE: The unit of the concentrations shown above is µmole/g. The conversion factor from µmole/g to µg/g is: M, where M is the average atomic weight of the element in g/mole (Section 7.4.1). The following equation can be used to convert the unit of the concentration. Be aware that samples with different isotopic abundance have different average atomic weights.

Concentration (µmole/g)$\times$ M = Concentration (µg/g)

NOTE: Although the species distribution of the isotopic spike is determined (Section 7.4), the above equations assume that each isotope-enriched spike is only in one species form to simplify the equations. This has been validated for ^{50}Cr(III) and ^{53}Cr(VI) spikes prepared using the procedures described in Section 7.3. For other speciation analysis, this assumption must be verified experimentally, or the distribution of the species in the isotope-enriched spikes must be taken into account.

NOTE: For the quantification of the single-spiked samples, the following equations are used:

$$C^{VI}_{Sample} = C^{VI}_X M_X$$

$$C^{VI}_S = C^{VI}_{Spike}/M^{VI}_S$$

$$C_X^{VI} = \frac{C_S^{VI} W_S}{W_X} \left(\frac{{}^{53}A_S^{VI} - R_{53/52}^{VI} \, {}^{52}A_S^{VI}}{R_{53/52}^{VI} \, {}^{52}A_X - {}^{53}A_X} \right)$$

where, C_S^{VI} and C_X^{VI} are the concentrations of the isotope-enriched spike and the sample in µmole/g, respectively. M_S and M_X are the average atomic weight of the isotope-enriched spike and the sample in g/mole, respectively. ${}^{53}A_S$ and ${}^{53}A_X$ are the atomic fraction of ${}^{53}Cr$ for the isotope-enriched spike and sample, respectively. ${}^{52}A_S$ and ${}^{52}A_X$ are the atomic fractions of ${}^{52}Cr$ for the isotope-enriched spike and sample, respectively. C_{spike} is the concentration of the isotope-enriched spike in µg/g.

NOTE: When isotope ${}^{50}Cr$ is used, substitute 53 with 50 in the above equations.

12.2.3 A computer program such as a spreadsheet can be developed to solve this set of second power, four variable equations. Solutions of the values for, C_X^{III}, C_X^{VI}, α and β are required. The following mathematics is a way to solve the equations iteratively. To assist the analyst a spreadsheet file with these preprogrammed equations has been placed on the internet (Reference 10). Additional discussion and alternate equations are also available.

To make the expression simpler, assume

$$C_X^{III} W_X = N_X^{III}, \; C_X^{VI} W_X = N_X^{VI}, \; C_S^{III} W_S = N_S^{III}, \; C_S^{VI} W_S = N_S^{VI}$$

At the beginning of the iteration, arbitrary values can be assigned to N_X^{VI} and α. For example, both of them are assigned as 0s. Now we need to know the expression of N_X^{III} and β. After careful derivation, we can get the following equations:

$$\begin{cases} (1-\alpha)\left(R_{50/52}^{III} \, {}^{52}A_X - {}^{50}A_X\right) N_X^{III} + \left[R_{50/52}^{III} \left({}^{52}A_X N_X^{VI} + {}^{52}A_S^{VI} N_S^{VI}\right) - \left({}^{50}A_X N_X^{VI} + {}^{50}A_S^{VI} N_S^{VI}\right)\right] \beta = \left(-R_{50/52}^{III} \, {}^{52}A_S^{III} + {}^{50}A_S^{III}\right) N_S^{III} (1-\alpha) \\ (1-\alpha)\left(R_{53/52}^{III} \, {}^{52}A_X - {}^{53}A_X\right) N_X^{III} + \left[R_{53/52}^{III} \left({}^{52}A_X N_X^{VI} + {}^{52}A_S^{VI} N_S^{VI}\right) - \left({}^{53}A_X N_X^{VI} + {}^{53}A_S^{VI} N_S^{VI}\right)\right] \beta = \left(-R_{53/52}^{III} \, {}^{52}A_S^{III} + {}^{53}A_S^{III}\right) N_S^{III} (1-\alpha) \end{cases}$$

These equations can be rewritten as:

$$\begin{cases} A_1 N_X^{III} + B_1 \beta = C_1 \\ A_2 N_X^{III} + B_2 \beta = C_2 \end{cases}$$

The solutions are

$$N_X^{III} = \frac{\begin{vmatrix} C_1 & B_1 \\ C_2 & B_2 \end{vmatrix}}{\begin{vmatrix} A_1 & B_1 \\ A_2 & B_2 \end{vmatrix}} \quad \text{and} \quad \beta = \frac{\begin{vmatrix} A_1 & C_1 \\ A_2 & C_2 \end{vmatrix}}{\begin{vmatrix} A_1 & B_1 \\ A_2 & B_2 \end{vmatrix}}$$

Use these two values in the following equations to solve N_X^{VI} and α

$$\begin{cases} (1-\beta)\left(R_{50/52}^{VI}\,{}^{52}A_X - {}^{50}A_X\right)N_X^{VI} + \left[R_{50/52}^{VI}\left({}^{52}A_X N_X^{III} + {}^{52}A_S^{III}N_S^{III}\right) - \left({}^{50}A_X N_X^{III} + {}^{50}A_S^{III}N_S^{III}\right)\right]\alpha = \left(-R_{50/52}^{VI}\,{}^{52}A_S^{VI} + {}^{50}A_S^{VI}\right)N_S^{VI}(1-\beta) \\ (1-\beta)\left(R_{53/52}^{VI}\,{}^{52}A_X - {}^{53}A_X\right)N_X^{VI} + \left[R_{53/52}^{VI}\left({}^{52}A_X N_X^{III} + {}^{52}A_S^{III}N_S^{III}\right) - \left({}^{53}A_X N_X^{III} + {}^{53}A_S^{III}N_S^{III}\right)\right]\alpha = \left(-R_{53/52}^{VI}\,{}^{52}A_S^{VI} + {}^{53}A_S^{VI}\right)N_S^{VI}(1-\beta) \end{cases}$$

Rewrite the equation as:

$$\begin{cases} A_3 N_X^{VI} + B_3\alpha = C_3 \\ A_4 N_X^{VI} + B_4\alpha = C_4 \end{cases}$$

again

$$N_X^{VI} = \frac{\begin{vmatrix} C_3 & B_3 \\ C_4 & B_4 \end{vmatrix}}{\begin{vmatrix} A_3 & B_3 \\ A_3 & B_3 \end{vmatrix}} \qquad \text{and} \qquad \alpha = \frac{\begin{vmatrix} A_3 & C_3 \\ A_4 & C_4 \end{vmatrix}}{\begin{vmatrix} A_3 & B_3 \\ A_4 & B_4 \end{vmatrix}}$$

Repeating the calculation, the variables N_X^{III} , N_X^{VI} , α and β will converge to constant values, and these values are the solution of the equations.

12.2.4 Results should be discarded when $\alpha + \beta > 80\%$ because the interconversion will be too extensive and cause inaccuracy and imprecision in the corrections. Samples should be respiked with the isotope-enriched spikes and analyzed, and the preservation should be improved to retard the conversion of the species.

12.2.5 If appropriate or required, calculate results for solids on a dry-weight basis as described in Section 12.1.3.

13.0 METHOD PERFORMANCE

13.1 Performance and use of IDMS as a definitive method in standard reference material certification has been well established in practice and in the literature. Review and discussion articles are referenced for performance criteria of this highly accurate method (References 1, 8, 9).

13.2 Accuracy, precision, and capability of SIDMS in correcting species interconversion are shown in Table 1. Table 2 and Table 3 compare data against Method 7196 analysis for Cr(VI) in chromium ore process residues and soil extracts. Table 1 demonstrates the ability of Method 6800 to correct for transformations of both Cr(VI) and Cr(III) in aqueous samples and also the magnitude of errors that may be expected when using other methods that are unable to determine the conversion of these species. Table 2 indicates a sample type where both the traditional 3060/7196 methods and 3060/6800 methods produced statistically similar data indicating confirmation between these two analytical methods. Table 3 demonstrates the correction necessary in some soil samples

where the sample matrix would cause a bias in more traditional methods. These bias corrections demonstrate the ability of Method 6800 to identify and correct for the degradation of a species during the measurement process.

13.3 The following documents may provide additional guidance and insight on this method and technique:

13.3.1 Javis, K. E.; Gray, A. L.; Houk, R. S. *Handbook of Inductively Coupled Plasma Mass Spectrometry*; Blackie: London, 1992.

13.3.2 Russ, G. P., III; Bazan, J. M. *Spectrochim. Acta, Part B* 1987, 42B, 49- 62.

14.0 Pollution Prevention

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quality and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of the first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better*. *Laboratory Chemical Management for Waste Reduction* available from the American Chemical Society.

15.0 Waste Management

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society.

16.0 References

1. Fasset, J. D.; Paulsen, P. J. Isotope Dilution Mass Spectrometry *Anal. Chem*. 1989, 61, 643A-649A.

2. Kingston, H. M. *Method of Speciated Isotope Dilution Mass Spectrometry*, US Patent Number: 5,414,259, 1995.

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7. Lu, Y.; Huo, D.; Kingston, H. M. "Determination of Analytical Biases and Chemical Mechanisms in the Analysis of Cr(VI) Using EPA Protocols, *(submitted Environ. Sci. Tech.,* 1998).

8. Bowers, G. N, Jr.; Fassett, J. D.; White, D. V. *Anal. Chem.* 1993, 65, 475R.

9. Moore, L. J.; Kingston, H. M.; Murphy, T. J. *Environ. Intern.* 1984, 10, 169.

10. Kingston, H. M.; Huo, D. (copywright 1998) SamplePrep Web™ [Homepage of SamplePrep Web™], [Online]. Available: http://www.sampleprep.duq.edu/sampleprep/ [1998, January 22].

17.0 Tables, Diagrams, Flowcharts, and Validation Data

The pages to follow contain Tables 1 through 3, Figures 1 through 5, and a method procedure flow diagram.

TABLE 1

ANALYSIS OF AN ARTIFICIALLY SYNTHESIZED WATER SAMPLE.
(Reference 6)

		Concentration (ng/g)		Conversion (%)	
Aliquot	Days after spiking	Cr(III)	Cr(VI)	Cr(III) to Cr(VI)	Cr(VI) to Cr(III)
1	1	69.8 ± 0.3	68.8 ± 0.3	4.87 ± 0.22	3.57 ± 0.03
	4	69.2 ± 0.6	69.4 ± 0.3	3.47 ± 0.11	11.9 ± 0.5
	13	70.5 ± 0.9	68.5 ± 0.4	2.80 ± 0.13	22.4 ± 0.2
2	1	69.6 ± 0.2	68.8 ± 0.4	17.6 ± 0.1	2.95 ± 0.02
	4	69.3 ± 0.7	69.6 ± 0.6	14.6 ± 1.3	11.4 ± 0.7
	13	70.7 ± 0.4	68.8 ± 0.3	12.8 ± 0.1	22.1 ± 0.3
3	1	69.8 ± 0.6	69.0 ± 0.2	23.8 ± 0.3	2.76 ± 0.08
	4	69.0 ± 0.8	69.6 ± 0.3	21.6 ± 0.2	10.2 ± 0.1
	13	70.4 ± 0.5	68.9 ± 0.8	17.6 ± 0.3	22.1 ± 0.1
True		69.67	68.63		

mean ± 95% confidence interval

Aliquots 1, 2 and 3 were from the same isotopically-spiked synthesized sample. These aliquots were treated in different ways to induce different degrees of interconversion between Cr(III) and Cr(VI). Measurements were done on different days to check the stability of the species during storage. Despite the different degrees of interconversion, the deconvoluted concentrations for both Cr(III) and Cr(VI) were always corrected successfully within experimental error to the true concentrations.

TABLE 2

CONCENTRATIONS OF CR(VI) IN COPR SAMPLES DETERMINED WITH METHOD 7196 AND SIDMS
(Reference 7)

sample	Method 7196		SIDMS	
	Conc. of Cr(VI) (µg/g)	Average (mean ±std)	Conc. of Cr(VI) (µg/g)	Average (mean ±std)
COPR1	1330	1410 ± 85	1373	1445 ± 70
	1410		1449	
	1500		1512	
COPR3	91.2	85.3 ± 5.2	93.9	88.8 ± 6.1
	81.5		82.1	
	83.1		90.4	
COPR4	408.9	407.8 ± 7.2	419.8	418.0 ± 9.2
	414.4		426.1	
	400.2		408.0	

COPR: chromite ore processing residue.
Method 3060 was used for Cr(VI) extraction.
Results obtained from SIDMS and Method 7196 are comparable for COPR samples.

TABLE 3

RECOVERY OF CR(VI) SPIKED INTO SOIL EXTRACTS
(Reference 7)

Sample	Mass of Soil (g)	Spiked ^{nat}Cr(VI)	Recovery (%)	
		(µg/g)	Method 7196	SIDMS
1	0	2.997	101 ± 0.4	100 ± 1.3
2	1.53	3.033	91.8 ± 1.7	100 ± 0.3
3	3.06	2.993	81.9 ± 1.1	101 ± 0.3
4	3.12	1.587	71.6 ± 2.5	99.3 ± 0.3

Results obtained from SIDMS and Method 7196 are incomparable for soil extracts due to the serious matrix effects resulting from the coexisting reducing agents in soil. Method 7196 is incapable of correcting conversion of Cr(VI) leading to low recoveries. Results are based on N = 3 with uncertainties expressed in standard deviation.

FIGURE 1

THE INFLUENCE OF THE DEAD TIME CORRECTION ON THE ISOTOPE RATIOS MEASURED WITH ICP-MS EQUIPPED WITH A CONTINUOUS DYNODE MULTIPLIER
Gain loss occurs when the count rate exceeds $5.8^{X}10^{5}$.

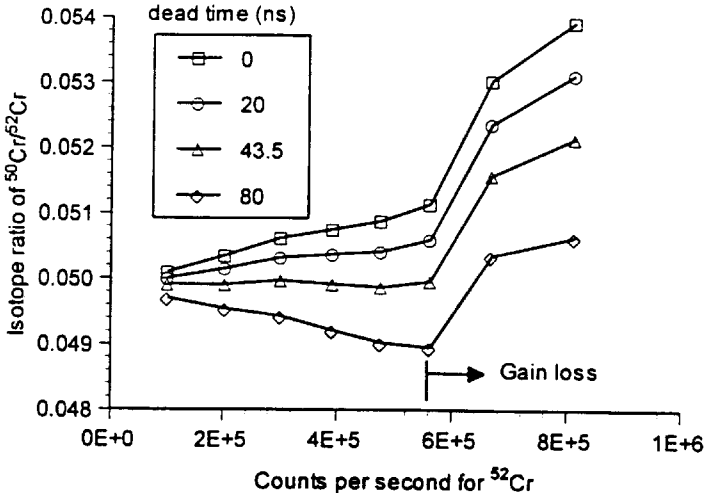


FIGURE 2

IDMS DETERMINATION OF VANADIUM IN CRUDE OIL. NUMBERS SHOWN ABOVE THE BARS ARE THE ATOMIC FRACTION
(Revised from Reference 1)

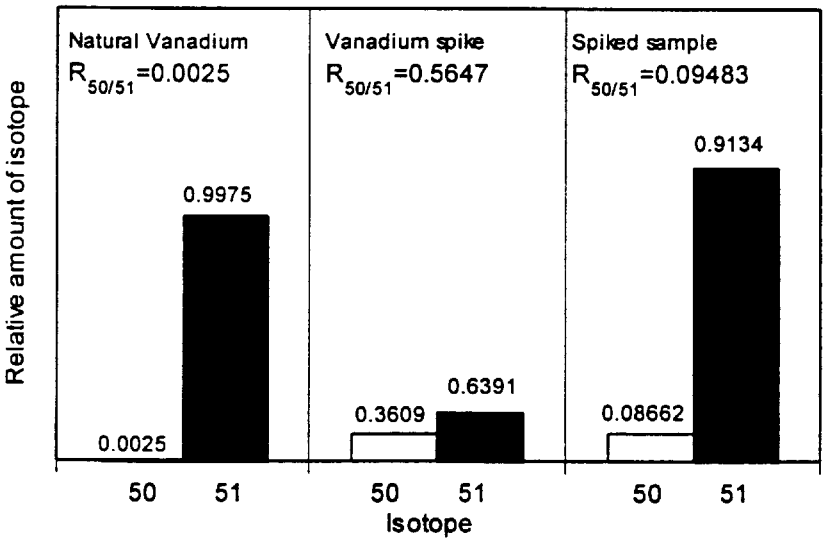


FIGURE 3

SEPARATION AND DETECTION OF CR(III) AND CR(VI) WITH ION-EXCHANGE CHROMATOGRAPHY COUPLED WITH AN ICP-MS
(Reference 5)

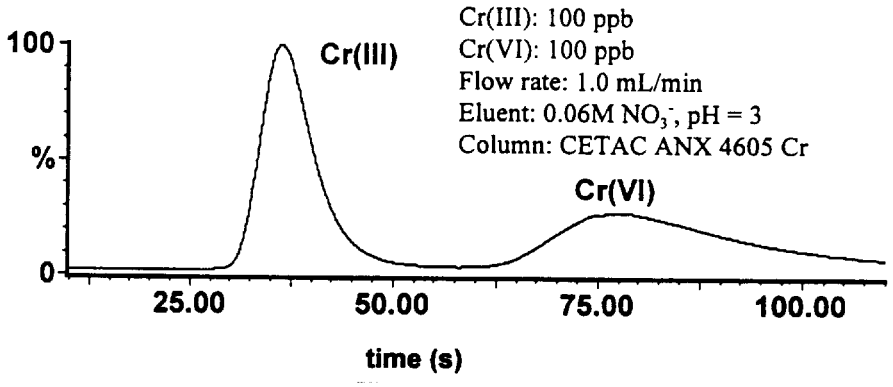


FIGURE 4
SEPARATION OF THE UNSPIKED SAMPLE AND ISOTOPICALLY SPIKED SAMPLE
(Reference 3)

(a): Chromatograms of a solution containing Cr(III) and Cr(VI) with natural isotopic abundance.
(b): Chromatograms of the same solution spiked with isotope-enriched spikes **^{50}Cr(III) and ^{53}Cr(VI) .**

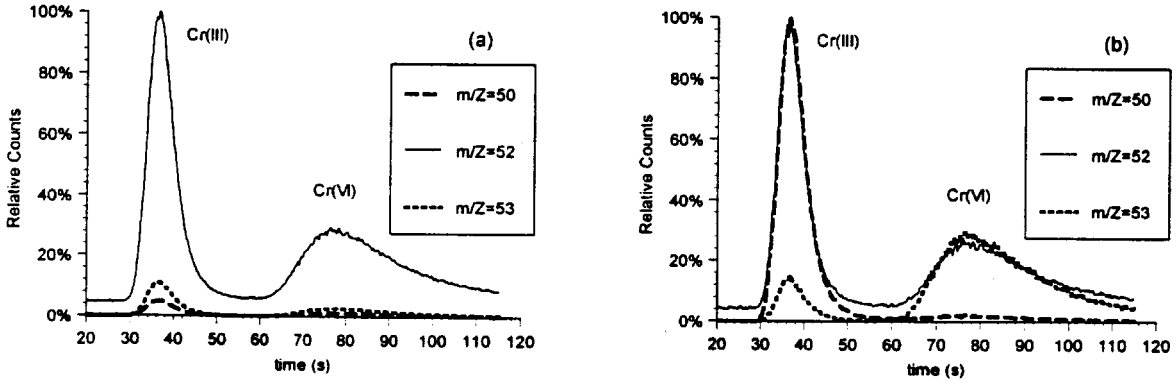
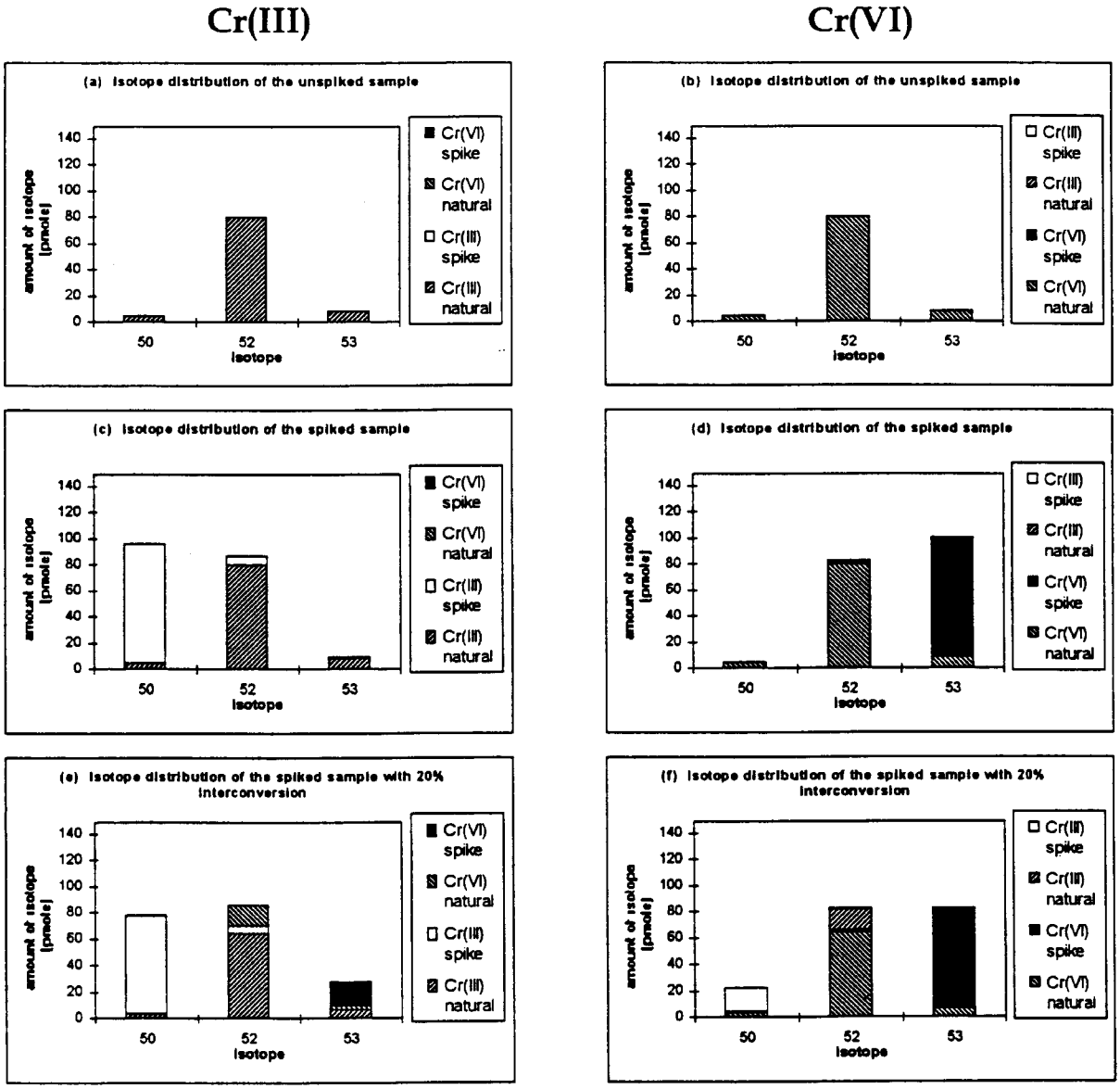


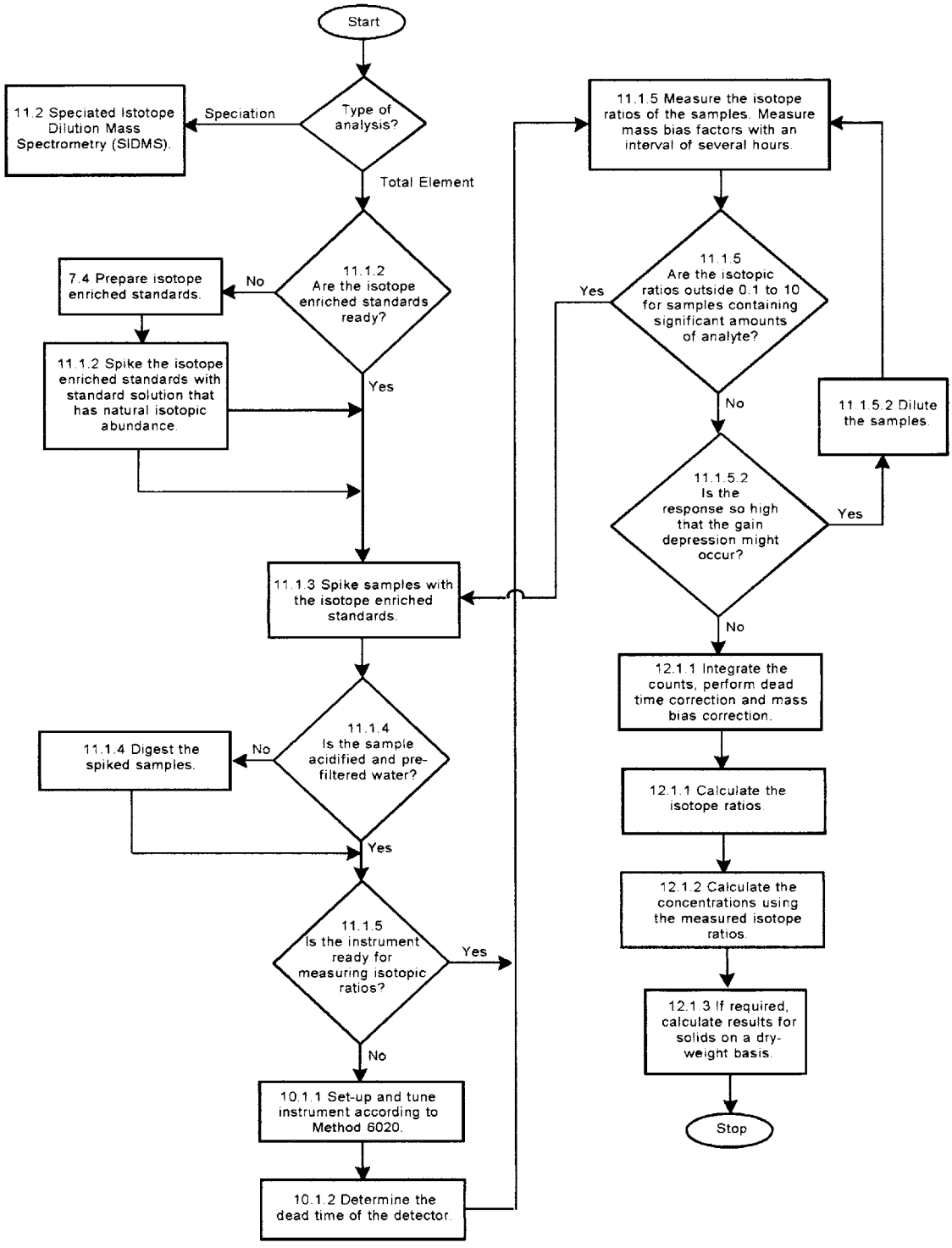
FIGURE 5

GRAPHIC CALCULATED ILLUSTRATION OF THE APPLICATION OF SIDMS TO THE SIMULTANEOUS DETERMINATION OF CR(III) AND CR(VI)



(a) and (b) show the initial natural isotopic abundance of species Cr(III) and Cr(VI) in a 50µl 200 ppb Cr solution in which the concentrations of both Cr(III) and Cr(VI) are 100 ppb. In (c) and (d), the sample is spiked with 100 ppb ^{50}Cr(III) (in which ^{50}Cr is enriched) and 100 ppb ^{53}Cr(VI) (in which ^{53}Cr is enriched), there is no interconversion between Cr(III) and Cr(VI). In (e) and (f), 20% of Cr(III) is converted to Cr(VI), and 20% of Cr(VI) is converted to Cr(III). Different degrees of interconversion results in different isotopic abundances, so the change of the relative isotopic abundance can be applied to the determination of the species and the degree of the interconversion.

ELEMENTAL AND SPECIATED ISOTOPE DILUTION MASS SPECTROMETRY: ISOTOPE DILUTION MASS SPECTROMETRY (IDMS)



ELEMENTAL AND SPECIATED ISOTOPE DILUTION MASS SPECTROMETRY: SPECIATED ISOTOPE DILUTION MASS SPECTROMETRY (SIDMS)